with a 0.25 in. × 10 ft long column packed with 15% OV17 on Chromosorb W. Preparative glpc was performed using an F & M Model 776 gas chromatograph equipped with a 0.75 × 80 in. long column packed with 15% OV17 on Chromosorb W.

Materials.—Eastman Grade 2-iodoaniline and 2-iodophenol were used without further purification. Chlorodiphenylborane was prepared by the method of Niedenzu, Beyer, and Dawson.[10] 2-Iodobenzenesulfonyl chloride was prepared by the method of Schwarzenbach and Egli.[11]

2-Iodothiophenol.—A solution of 200 g (0.88 mol) of stannous chloride dihydrate in 250 ml of concentrated hydrochloric acid was treated over 10 min with a solution of 50 g (0.17 mol) of 2-iodobenzenesulfonyl chloride in 250 ml of acetic acid. The solution was stirred on a steam bath for 2 hr, then steam distilled. The distillate was extracted with dichloromethane, and the extract dried and evaporated to yield the crude thiol. Distillation yielded the pure thiol, 22 g, 56%, bp 117–120° (10 mm) [lit.[11] bp 119.5° (11 mm)]. It was stored at 0° over zinc dust under nitrogen.

Photocyclizations.—The horizontal thin-film photochemical reactor described earlier[12] was used for the preparation of the boron-containing compounds. The apparatus was thoroughly dried under vacuum for 1 hr and filled with dry nitrogen. The iodo compound was then introduced into the flask and the apparatus evacuated and filled with dry nitrogen several times. Approximately 600 ml of dry cyclohexane was then distilled directly from lithium aluminum hydride under nitrogen into the flask. The chlorodiphenylborane and the 2,6-lutidine were injected into the flask, and the contents mixed for 1 hr at room temperature by rotating the flask. The resulting solution was then irradiated using a Hanovia 100-W 608A-36 lamp in a quartz insert. The progress of the reaction was followed by withdrawing 100-μl samples of the photolysis solution. The sample was then diluted with 3 ml of solvent and examined by ultraviolet spectroscopy. Compound **1a** shows a characteristic band at 329 mμ (ε 10,600), **1b** shows a band at 323 mμ (ε 6300), and **1c** shows a band at 338 mμ (ε 7850). When no increase in the intensity of the long-wavelength band was observed, the contents of the flask were removed and washed in sequence with water, dilute hydrochloric acid, water, dilute sodium thiosulfate solution, and water. (Solutions of **1a** were also washed with dilute sodium hydroxide solution.) The organic layer was dried and evaporated to yield the crude product.

10-Phenyl-10,9-borazarophenanthrene (1a).—The crude product from run 5 (see Table I) crystallized as prisms from ligroin (bp 63–75°), 0.65 g, 51%, mp 106–108°, and was identical with an authentic sample.[4]

10-Phenyl-10,9-boroxarophenanthrene (1b).—The crude product (run 9, Table I) was purified by preparative glpc at 280° to yield the pure compound as a white solid, mp 80–82°, 0.35 g, 31%, identical with an authentic sample.[7]

10-Phenyl-10,9-borathiarophenanthrene (1c).—The crude product (run 12, Table I) crystallized from ligroin (bp 63–75°) in pale yellow prisms, 0.7 g, 50%, mp 129–130°.

Anal. Calcd for $C_{18}H_{13}BS$: C, 79.5; H, 4.8; B, 4.0; S, 11.8; mol wt, 272. Found: C, 79.2; H, 5.0; B, 4.0; S, 11.7; mol wt, 272 (mass spectrum).

Registry No.—**1a,** 19393-10-3; **1b,** 19374-73-3; **1c,** 19374-74-4.

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Observations on the Mechanism of Addition of Iodine Isocyanate to Unsaturated Compounds[1,2]

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Addition of iodine isocyanate to unsaturated compounds has been studied under competitive reaction conditions with pairs of olefins using preformed solutions of iodine isocyanate and also generating it *in situ*. Reactivity series are obtained which not only differ from each other but also from a series derived from kinetic studies (single olefins used) with *in situ* generated iodine isocyanate. When preformed solutions of iodine isocyanate are used the rate depends primarily on its concentration and that of the unsaturated compound, and is approximated by second-order kinetics. When iodine isocyanate is generated *in situ* in the presence of the unsaturated compound, complexation with iodine can play a major role in the mechanism depending on the complexation ability of the unsaturated compound. With poorly complexing but reactive olefins, for example, 2,3-dimethyl-2-butene, the reaction approaches the limiting rate of formation of iodine isocyanate. Most unsaturated compounds, however, react in part with iodine isocyanate directly and in part as iodine–olefin complexes with silver cyanate to form the observed vicinal iodoisocyanates.

In previous articles[4,5] we discussed the relative rates of addition of iodine isocyanate, generated *in situ* from iodine and silver cyanate, to unsaturated compounds. These results showed that *in situ* addition of iodine isocyanate occurs in an electrophilic manner, confirming the same observation, based on stereochemical considerations, by Hassner and Heathcock[6] and Drefahl, Ponsold and Köllner.[7]

Studies by Rosen and Swern[8] have shown that homogeneous, preformed solutions of iodine isocyanate also react in an electrophilic manner. We have now extended these studies to include the competitive reaction of pairs of olefins with preformed and *in situ* generated iodine isocyanate.

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(1) Pseudohalogens. VI. For V, see H. Hamann and D. Swern, *Tetrahedron Lett.*, No. 28, 3303 (1966).

(2) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. The authors wish to acknowledge the partial support of this work by U. S. Public Health Service Research Grants CA-07803 and CA-07174 of the National Cancer Institute.

(3) Work submitted by C. G. G. in partial fulfillment of the requirements for the Ph.D. degree, and by S. R. for the Master's degree, Temple University, Feb 1967.

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TABLE I

SUMMARY OF COMPETITIVE REACTIONS BETWEEN PAIRS OF OLEFINS AND *in situ* GENERATED IODINE ISOCYANATE (solvent, 100.0 ml of anhydrous ether)

Olefins used							
More reactive olefin	Amt, mol	Less reactive olefin	Amt, mol	AgOCN, mol	I_2, mol	Molar ratio of total olefins/I_2	Reactivity ratio faster/slower
trans-3-Hexene[a]	0.01121	1-Octene	0.01110	0.01341	0.00689	3.24	2.89
Cyclohexene[b]	0.01635	1-Hexene	0.01274	0.01349	0.00671	4.34	100/0
Cyclohexene[b]	0.01607	*trans*-3-Hexene	0.01277	0.01334	0.00692	5.01	≥12.7
Cyclohexene[b]	0.01615	*trans*-3-Hexene	0.01282	0.01908	0.00985	2.94	2.59
Cyclohexene[b,c]	0.01604	*trans*-3-Hexene	0.01273	0.01336	0.00694	4.14	2.53
Cyclopentene[b]	0.01744	Cyclohexene	0.01593	0.01339	0.00690	4.84	6.85
Cyclopentene[b,d]	0.01715	Cyclohexene	0.01726	0.01346	0.00689	5.00	3.55

[a] Internal standard, *n*-heptane. [b] Internal standard, benzene. [c] In this experiment, the iodine was added last to start the reaction. [d] In this experiment, the iodine and cyclohexene were equilibrated for 24 hr at −20°. The cyclopentene was added 1 hr before the addition of AgOCN which started the reaction.

TABLE II

COMPOSITION AND REACTIVITY OF COMPETITIVE REACTIONS WITH PERFORMED IODINE ISOCYANATE SOLUTIONS

Olefins used					
More reactive olefin	*M*	Less reactive olefin	*M*	Iodine isocyanate, *M*	Reactivity ratio faster/slower
trans-3-Hexene	0.097	1-Octene	0.088	0.057	4.1
trans-3-Hexene	0.136	Cyclohexene	0.171	0.075	1.8
2,3-Dimethyl-1-butene	0.143	Cyclohexene	0.139	0.040	1.4
2,3-Dimethyl-2-butene	0.163	2-Methyl-2-pentene	0.174	0.047	2.3
2-Methyl-2-pentene	0.154	2,3-Dimethyl-1-butene	0.142	0.043	≥10
Cyclopentene	0.189	Cyclohexene	0.165	0.060	≥10

Experimental Section

A. Competitive Reactions Using *in situ* Generated Iodine Isocyante.—The conditions and results of competitive reactions of *in situ* generated iodine isocyanate with pairs of olefins present in large excess are summarized in Table I. Reactions were run at −20 to −30°. The reaction vessel was a 100-ml four-necked flask fitted with an electrically driven Teflon-blade stirrer, a thermometer and a drying tube. The fourth opening was sealed with a rubber septum through which samples were removed for analysis by gas–liquid partition chromatography. All glpc analyses were obtained on a F & M Scientific Model 500 chromatograph using a 20-ft column of 15% Apiezon L on 70/80 mesh Anakrom ABS, with detection by thermal conductivity.

The accurately weighed amount of iodine was placed in the reaction flask, dissolved in ether and cooled to reaction temperature in a dewar flask. A known amount of a mixture of the two olefins and an internal standard for glpc calibration was then added and five to eight initial glpc determinations were made with 3–5 μl of solution. Silver cyanate was then added in one portion to start the reaction. Progress of the reaction was followed by periodic glpc analysis. These competitive *in situ* reactions were very slow and only the final results, after 24 hr, are summarized in Table I as the reactivity ratios. The results are the average of five to eight glpc determinations. In all cases, the concentrations of both olefins were determined by reference against a common internal standard. The reaction products could not be determined as they do not elute under the conditions used.

Since slightly different molarities of each olefin were used in these experiments, the reactivity ratios were computed as ratios of the percentages of each olefin that reacted.

B. Competitive Reactions Using Preformed Solutions of Iodine Isocyanate.—Preformed solutions were prepared in the usual manner.[8] After initial glpc measurements were made on the mixture of the two olefins with internal standard, a known amount of this mixture was added to the preformed iodine isocyanate solution. The composition of these homogeneous competitive experiments is shown in Table II.

Samples for glpc determination were removed periodically and the titer of iodine isocyanate was also determined.[8] Reactions with preformed iodine isocyanate were very rapid and essentially complete in less than 30 min. The method of calculation of the reactivity ratios in Table II was the same as with the *in situ* systems.

Results

The reactivity ratios of Table II for competitive reactions with preformed iodine isocyanate have been converted into a relative reactivity scale, shown in Table III, with the value for cyclohexene arbitrarily set at 100. The relative ranking of cyclopentene and 2-methyl-2-pentene can not be definitely established from the available data but 2,3-dimethyl-2-butene is 2.3 times as reactive as 2-methyl-2-pentene. These results constitute an electrophilic series similar to that determined previously from kinetic studies with *in situ* generated iodine isocyanate.[4,5]

TABLE III

COMPARISON OF THREE DIFFERENT RELATIVE REACTIVITY SERIES FOR THE ADDITION OF IODINE ISOCYANATE TO OLEFINS

	Reaction method		
Olefin	Competitive preformed[a]	Competitive *in situ*[b]	Kinetic *in situ*[d]
2,3-Dimethyl-2-butene	>3200		3800
2-Methyl-2-pentene	>1400		
Cyclopentene (C)	>1000	685	221
trans-3-Hexene (A)	180	≤7.9	571
2,3-Dimethyl-1-butene	140		
Cyclohexene (B)	100	100	100
1-Octene	44	≤2.7	50[c]

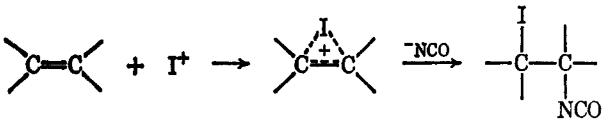
[a] From Table II. [b] From Table I. [c] 1-Hexene. [d] See ref 4 and 5.

An entirely different series results when the data from Table I for competitive reactions with *in situ* generated iodine isocyanate are compiled into a relative reactivity series shown in Table III. The series previously obtained in kinetic studies with *in situ* generated iodine isocyanate[4,5] is also shown in Table III.

Discussion

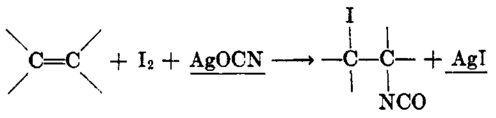
Comparison of the Different Iodine Isocyanate Series. Although each reactivity series is readily duplicated and generally conforms to an electrophilic pattern, the variation among them with the method of determining the series suggests differences in reaction mechanism. From a mechanistic standpoint, the simplest series is obtained from competitive studies of the addition of preformed solutions of iodine isocyanate to olefins. In the other cases, the iodine isocyanate is generated while the reaction is in progress and this might be expected to lead to complications. We have previously shown that generation of iodine isocyanate is a relatively slow process, in the absence of an olefin.[8]

The reaction of preformed iodine isocyanate can be represented by the given sequence. Preliminary kinetic data[8] on this system indicate that the reaction follows second-order kinetics. In general, rate of addition of preformed iodine isocyanate increases with the number of electron-donating alkyl groups attached to the double bond. Thus the reactivity increases with the ability to form more highly stabilized carbonium ions.



The competitive and kinetic *in situ* systems, however, give reactivity series that are different from each other and from that obtained with preformed iodine isocyanate. These differences are most apparent in the reactivity ranking (slowest to fastest) of *trans*-3-hexene (A), cyclohexene (B), and cyclopentene (C): competitive, preformed, B, A, C; competitive, *in situ*, A, B, C; kinetic, *in situ*, B, C, A.

The over-all equation for *in situ* reactions is given.



$$>C{=}C< + I_2 + \underline{AgOCN} \longrightarrow -\overset{I}{\underset{|}{C}}-\underset{NCO}{C}- + \underline{AgI}$$

One of the steps is the generation of iodine isocyanate, but side reactions are also possible in this system. Olefins are known to form complexes with both silver and iodine, and complex formation would certainly result in differences in apparent reactivity.

The formation of diiodides from these complexes would introduce large errors into equilibrium constants and into any work on kinetics and competitive reactions. Diiodide formation can occur but is rapid only in the presence of light.[9-12] This problem was minimized in our studies by excluding light. Thus, we obtained yields of the iodine isocyanate adduct with cyclohexene in excess of 90% even though cyclohexene reacts relatively slowly in the *in situ* systems.

These considerations are consistent with the formation of an iodine–olefin complex as an important part of the reaction mechanisms. Numerous reactions can be visualized as important in the over-all reaction, including the formation and reaction of iodine–olefin complexes and the formation and reaction of iodine isocyanate, but the heterogeneous system is too complex for kinetic analysis.[13]

Rosen and Swern[8] have shown that *trans*-3-hexene reacts very rapidly with solutions of iodine isocyanate. The relative reactivities determined here show that 2,3-dimethyl-2-butene is at least 18 times more reactive than *trans*-3-hexene, and suggests that 2,3-dimethyl-2-butene reacts with iodine isocyanate as rapidly as it is generated. The rate of generation of iodine isocyanate is the limiting rate for the reaction in which *in situ* generated iodine isocyanate is added to this olefin.

Conclusions

The addition of iodine isocyanate, whether from preformed solutions or generated *in situ*, proceeds in an electrophilic manner. The reaction rate is much faster with preformed solutions. From a synthesis standpoint the use of preformed solutions of iodine isocyanate might prove advantageous when working with olefins that react slowly, such as 1 olefins. With relatively rapidly reacting olefins, such as *trans*-3-hexene, the *in situ* method is probably more convenient since the *total* time (generation of iodine isocyanate plus addition) is about the same.

Registry No.—Iodine isocyanate, 3607-48-5.

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